Multiscale Simulations

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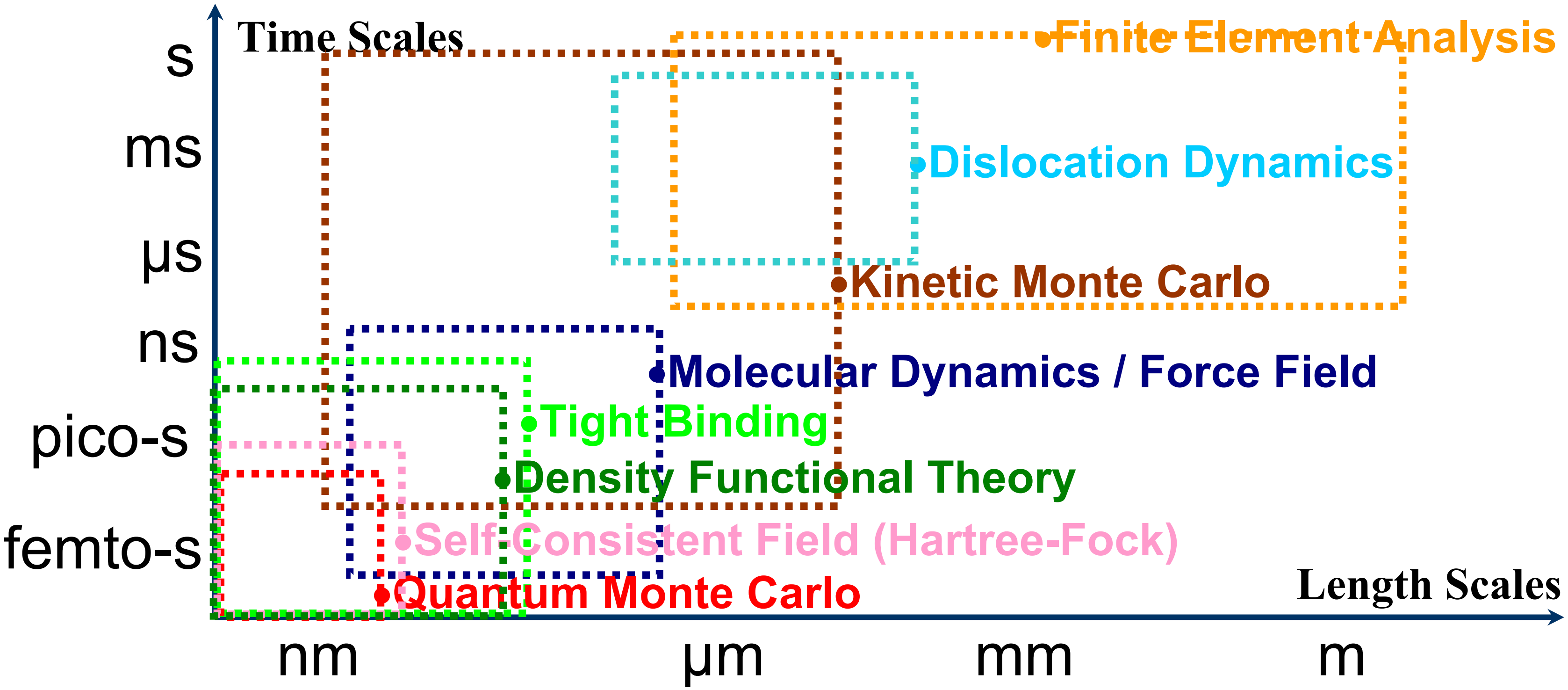
Topics

- DFT-MD coupling
  - First-Principles Molecular Dynamics
- DFT-KMC coupling
  - on-the-fly KMC simulation
- MD-FEM coupling
  - Quasicontinuum method
  - Coarse-Grained Molecular Dynamics

Modeling & Simulation at Multiple Scales



Various methods used to simulate at different length and time scales

Zoo of Multiscale Simulation Methods

- First-principles MD (quantum-atomistic coupling)
  - Ehrenfest MD
  - Born-Oppenheimer MD
  - Car-Parrinello MD
- on-the-fly KMC (DFT-KMC coupling)
- QM/MM coupling

- Mathematical Homogenization
- Heterogeneous Multiscale Method
- Multiscale FEM

- quasi-continuum
- coarse-grained molecular dynamics
- variational multiscale method
- concurrent coupling
- coupled atomistic/discrete-dislocation
- adaptive multiscale modeling,
- bridging scale method
- bridging domain method
- DD/FEM coupling
- TB/MD/FEM coupling
- *…<new species born each year>…*

First-Principles Molecular Dynamics

- The major idea is to replace the "predefined potentials" in classical molecular dynamics (MD) by first-principles electronic structure calculation on-the-fly (i.e. keep electronic variables as active degrees of freedom in MD).

  - The Algorithm:
    1. solve the electronic structure problem for a set of ionic coordinates
    2. evaluate forces
    3. move atoms
    4. repeat

Classical MD

- Based on Newtonian dynamics

  $$M_I \ddot{\mathbf{R}}_I(t) = \mathbf{F}_I(t) = -\nabla_I V_e^{approx}\left(\{\mathbf{R}_I(t)\}\right)$$

  where

  $$V_e^{approx}\left(\{\mathbf{R}_I(t)\}\right) = \sum_{I=1}^{N} V^{(1)}\left(\mathbf{R}_I(t)\right) + \sum_{I<J} V^{(2)}\left(\mathbf{R}_I(t), \mathbf{R}_J(t)\right) + \sum_{I<J<K} V^{(3)}\left(\mathbf{R}_I(t), \mathbf{R}_J(t), \mathbf{R}_K(t)\right) + \cdots$$

  is a *few-body-additive-interaction* ***approximation*** of the true potential energy surface.
- The electrons follow adiabatically the classical nuclear motion and can be integrated out so that the nuclei evolve on a single global Born-Oppenheimer potential energy surface.
- *A priori* construction of the global potential energy surface suffers from the ‘dimensionality bottleneck’.

Time-Dependent Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \Phi\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t\right) = \mathcal{H}\Phi\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t\right)$$

where

$$\mathcal{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} + \sum_{I<J}\frac{Z_I Z_J e^2}{\left|\mathbf{R}_I - \mathbf{R}_J\right|} - \sum_{I,i}\frac{Z_I e^2}{\left|\mathbf{r}_i - \mathbf{R}_I\right|}$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + V_{n-e}\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \mathcal{H}_e\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right)$$

- Total wavefunction can be decomposed as

$$\Phi\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t\right) \approx \Psi\left(\{\mathbf{r}_i\};t\right)\chi\left(\{\mathbf{R}_I\};t\right)\exp\left(\frac{i}{\hbar}\int_{t_0}^{t} dt'\,\tilde{E}_e(t')\right)$$

with a phase factor

$$\tilde{E}_e = \int d\mathbf{r}\, d\mathbf{R}\, \Psi^* \chi^* \mathcal{H}_e \Psi \chi$$

Ehrenfest Molecular Dynamics

- Simultaneously solve

$$
\begin{aligned}
M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I V_e^E\left(\{\mathbf{R}_I(t)\}\right) \\
&= -\nabla_I \left\langle \Psi \mid \mathcal{H}_e \mid \Psi \right\rangle \\
&= -\nabla_I \int d\mathbf{r} \Psi^* \mathcal{H}_e \Psi
\end{aligned}
$$

$$
\begin{aligned}
i\hbar \frac{\partial}{\partial t} \Psi &= \mathcal{H}_e \Psi \\
&= -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{n-e}\left(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}\right) \Psi
\end{aligned}
$$

Born-Oppenheimer Molecular Dynamics

- In *ground state* BOMD, the *time-independent* electronic structure problem is solved self-consistently from each time for a given configuration of nuclei

$$\boxed{M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \left\langle \Psi_0 \,|\, \mathcal{H}_e \,|\, \Psi_0 \right\rangle}$$

$$\boxed{\mathcal{H}_e \Psi_0 = E_0 \Psi_0}$$

- Electrons are *explicitly* set to be fully relaxed for a given configuration of nuclei, in contrast to Ehrenfest MD where electron relaxation is *implicit* by solving the time-dependent Schrödinger equation.

BOMD with HF-SCF

- Assuming single Slater determinant $\Psi_0 = \det\{\psi_j\}$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\psi_j\}} \langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0 \rangle$$

- Constrained (orthonormal orbitals) minimization

$$\min_{\{\psi_j\}} \langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0 \rangle \qquad s.t.\ \langle \psi_i \mid \psi_j \rangle = \delta_{ij}$$

- Define Lagrangian

$$\mathcal{L} = \langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} (\langle \psi_i \mid \psi_j \rangle - \delta_{ij})$$

- The necessary condition of optimality $\partial \mathcal{L} / \partial \psi_j = 0$ leads to Hartree-Fock equations

$$\mathcal{H}_e^{HF} \psi_j = \sum_i \Lambda_{ij} \psi_j$$

- Then the new equations of motion are

$$\boxed{M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\psi_j\}} \langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0 \rangle}$$

$$\boxed{\mathcal{H}_e^{HF} \psi_j = \sum_i \Lambda_{ij} \psi_j}$$

BOMD with DFT

- Based on the *Hellmann-Feynman theorem*, MD force is

$$\mathbf{F}_I = -\nabla_I \left\langle \Psi_0 \,|\, \mathcal{H}_e \,|\, \Psi_0 \right\rangle = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 \,|\, \mathcal{H}_e \,|\, \Psi_0 \rangle = -\langle \Psi_0 \,|\, \frac{\partial \mathcal{H}_e}{\partial \mathbf{R}} \,|\, \Psi_0 \rangle$$

- Recall

$$\mathcal{H}_e\left(\{\mathbf{r}_i\},\{\mathbf{R}_I\}\right) = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I<J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I,i}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$

- The force is computed by DFT as

$$\mathbf{F}_I = -\langle \Psi_0 \,|\, \frac{\partial \mathcal{H}_e}{\partial \mathbf{R}} \,|\, \Psi_0 \rangle =$$

$$= -\sum_J \nabla_I \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \sum_i \int \Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_M)\nabla_I \frac{Z_R e^2}{|\mathbf{r}_i - \mathbf{R}_I|}\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_M)\,d\mathbf{r}_1\ldots d\mathbf{r}_M$$

$$= -\sum_J \nabla_I \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \int \rho(\mathbf{r})\nabla_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}d\mathbf{r}$$

BOMD with DFT

1. Fix positions of nuclei $\{\mathbf{R}_1,\ldots,\mathbf{R}_N\}$, solve DFT equations self-consistently;

$$\left[-\frac{1}{2}\nabla^2-\sum_I\frac{Z_Ie^2}{|\mathbf{r}-\mathbf{R}_I|}+\int\frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})$$

$$\rho(\mathbf{r})=\sum_i f_i\,|\psi_i(\mathbf{r})|^2$$

2. Find electrostatic force on each atom;

$$\mathbf{F}_I=-\sum_J\nabla_I\frac{Z_IZ_Je^2}{|\mathbf{R}_I-\mathbf{R}_J|}+\int\rho(\mathbf{r})\nabla_I\frac{Z_Ie^2}{|\mathbf{r}-\mathbf{R}_I|}d\mathbf{r}$$

3. Perform a time step and find new positions of nuclei;

$$M_I\ddot{\mathbf{R}}_I(t)=\mathbf{F}_I$$

4. Repeat;

Drawbacks of BOMD

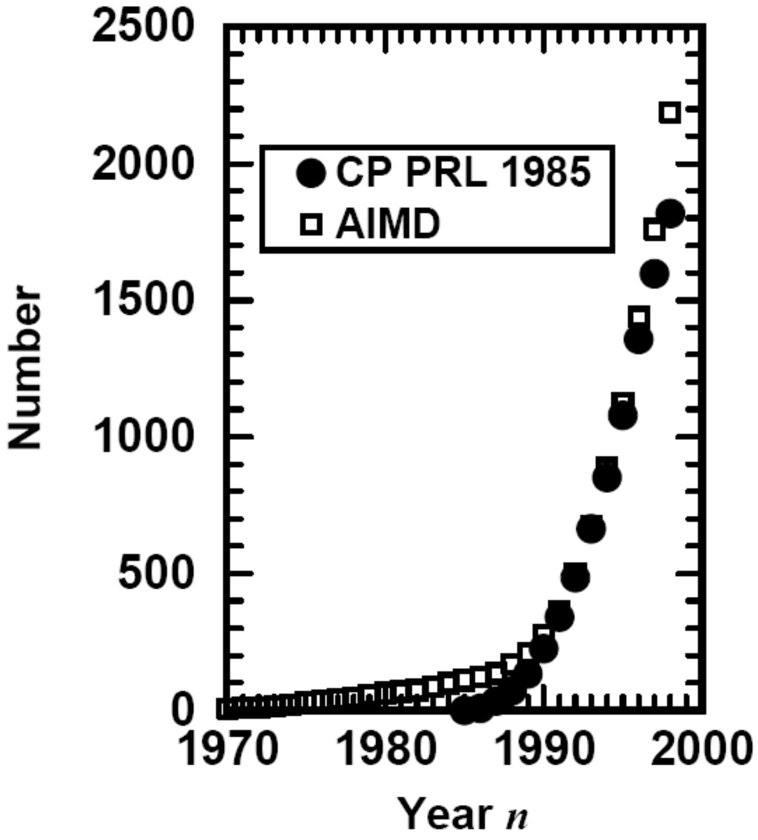
- The need to fully relax electronic subsystem while moving the atoms makes it computationally expensive.
- Full self-consistency at each MD step may not be necessary, especially when system is far from its equilibrium, since one simply needs a rough idea of the force field for a given atomic configuration

Car-Parrinello Molecular Dynamics

R. Car and M. Parrinello (1985) Unified approach for molecular dynamics and density-functional theory. *Phys. Rev. Lett.* **55**: 2471.

Publication and citation analysis:
□: number of publications which appeared up to the year *n* that contain the keyword "ab initio molecular dynamics" (or synonyma "first-principles MD", Car-Parrinello simulations" etc.) in title, abstract or keyword list.

●: number of publications which appeared up to the year n that cite the 1985 paper by Car and Parrinello



Car-Parrinello Lagrangian

- Car and Parrinello (1985) postulated the Lagrangian

$$\mathcal{L}_{CP} = \underbrace{\sum_I \frac{1}{2} M_I \ddot{\mathbf{R}} + \sum_i \frac{1}{2} \mu_i \langle \dot{\psi}_i \mid \dot{\psi}_i \rangle}_{\textit{Kinetic Energy}} - \underbrace{\langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0 \rangle}_{\textit{Potential Energy}} + \underbrace{\sum_{ij} \Lambda_{ij} (\langle \psi_i \mid \psi_i \rangle - \delta_{ij})}_{\textit{Constraints}}$$

where μ_i's are fictitious "masses" for the dynamics of orbitals ψ_i's .

Car-Parrinello Equations of Motion

- From Euler-Lagrange differential equations in classical mechanics (to ensure $\delta\int \mathcal{L}_{CP}(\mathbf{R}_I,\dot{\mathbf{R}}_I,\psi_i,\dot{\psi}_i;t)dt = 0$)

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{CP}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{CP}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}_{CP}}{\partial \dot{\psi}_i} = \frac{\partial \mathcal{L}_{CP}}{\partial \psi_i}$$

- Car-Parrinello equations of motion is derived as

$$\boxed{M_I\ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I}\langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0\rangle + \frac{\partial}{\partial \mathbf{R}_I}\left\{\text{constraints}(\{\psi_i\},\{\mathbf{R}_I\})\right\}}$$

$$\boxed{\mu_i\ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i}\langle \Psi_0 \mid \mathcal{H}_e \mid \Psi_0\rangle + \frac{\delta}{\delta \psi_i}\left\{\text{constraints}(\{\psi_i\},\{\mathbf{R}_I\})\right\}}$$

CPMD with DFT

- Car-Parrinello equations of motion

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E_{DFT}[\{\psi_i\},\{\mathbf{R}_I\}]}{\partial \mathbf{R}_I}$$

$$= \int \rho(\mathbf{r},t)\nabla_I \frac{Z_I e^2}{|\mathbf{r}-\mathbf{R}_I(t)|} d\mathbf{r}$$

$$\mu_i \ddot{\psi}_i(\mathbf{r},t) = -\frac{\delta E_{DFT}[\{\psi_i\},\{\mathbf{R}_I\}]}{\delta \psi_i(\mathbf{r},t)} + \sum_j \varepsilon_{ij}\psi_j(\mathbf{r},t)$$

$$= -\mathcal{H}_{DFT}\psi_i(\mathbf{r},t) + \sum_j \varepsilon_{ij}\psi_j(\mathbf{r},t)$$

Verlet algorithm in CPMD Orbital Dynamics

- First, a verlet step ignoring orthogonality constraint

$$\tilde{\psi}_i(t+\Delta t) = 2\psi_i(t) - \psi_i(t-\Delta t) + \frac{(\Delta t)^2 \mathcal{H}_{DFT}\psi_i(t)}{\mu_i}$$

- Then, restore orthogonality

$$\psi_i(t+\Delta t) = \tilde{\psi}_i(t+\Delta t) + \xi \cdot \psi_i(t)$$

- Computationally dynamics is applied to c_i's in the reciprocal space with Kohn-Sham orbitals

$$\psi_i(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\|\Omega\|}} \sum_{\mathbf{G}} c_i(\mathbf{G},\mathbf{k}) \exp\left[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r} \right]$$

CPMD Code

- The CPMD code is a planewave implementation of DFT for first-principles molecular dynamics
- First version by Jürg Hutter at IBM Zurich Research Lab with dozens of other contributors
- The code is copyrighted jointly by IBM Corp and by Max Planck Institute, Stuttgart
- It is distributed free of charge to non-profit organizations (http://www.cpmd.org/)

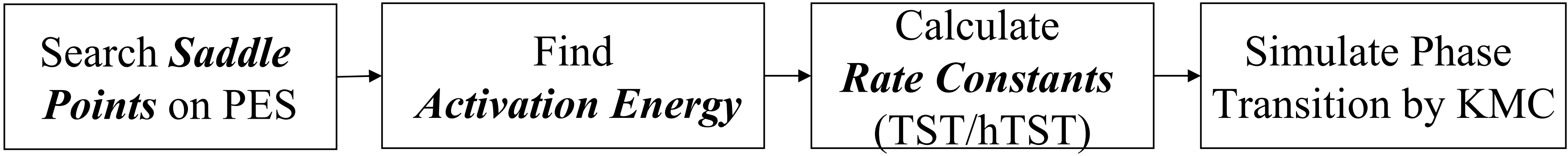
CPMD capabilities

- Wavefunction optimization: direct minimization and diagonalization
- Geometry optimization: local optimization and simulated annealing
- Molecular dynamics: NVE, NVT, NPT
- Path integral MD
- Response functions
- Excited states
- Time-dependent DFT (excitations, MD in excited states)
- Coarse-grained non-Markovian metadynamics
- Wannier, EPR, Vibrational analysis
- QM/MM

- See on-line manual at: http://cpmd.org/documentation/cpmd-html-manual

On-the-fly KMC

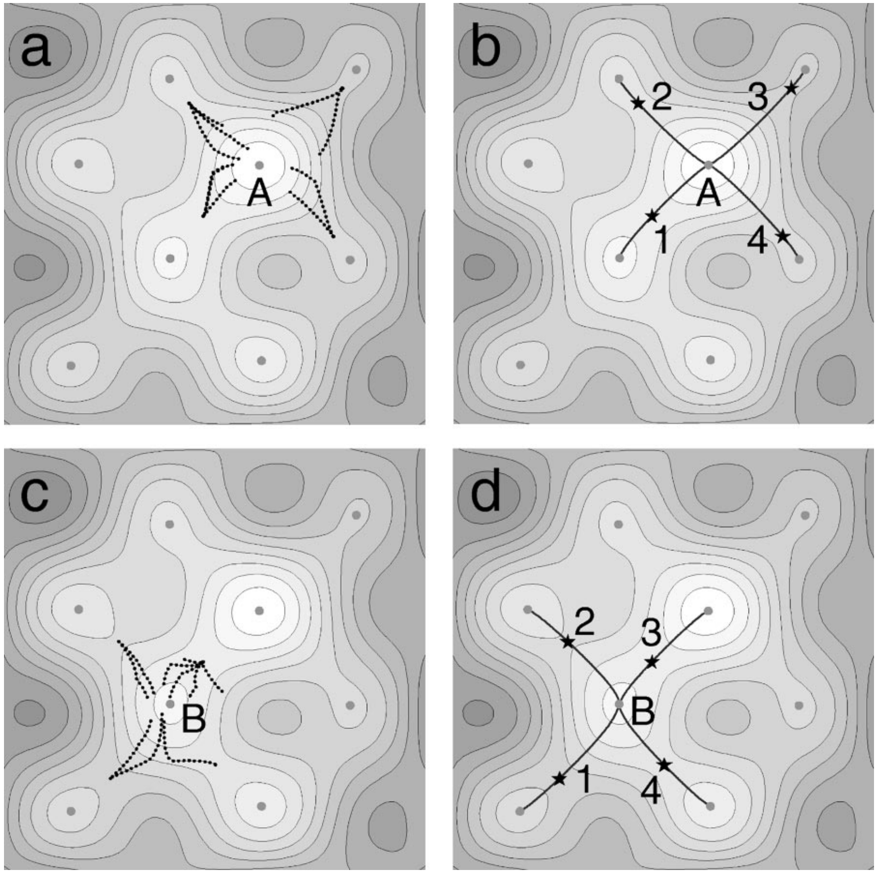
- Searching saddle points on the potential energy surface (PES) on-the-fly while performing KMC simulation



Search ***Saddle Points*** on PES → Find ***Activation Energy*** → Calculate ***Rate Constants*** (TST/hTST) → Simulate Phase Transition by KMC

On-the-fly KMC

1. Start from a minimum configuration;
2. Randomly generate a set of configurations around the minimum and search the saddle points by the Dimer method;
3. Locate the saddle points connect to the minimum;
4. Insert the new events and propensities in the event table in KMC and simulate one step;
5. Repeat;



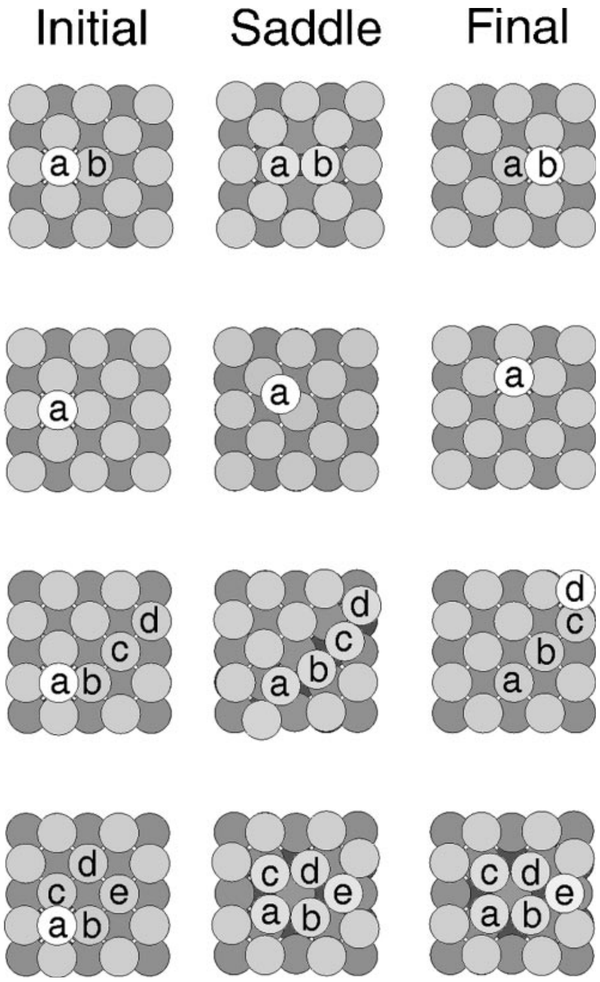
Diffusion of adatom on Al(100)

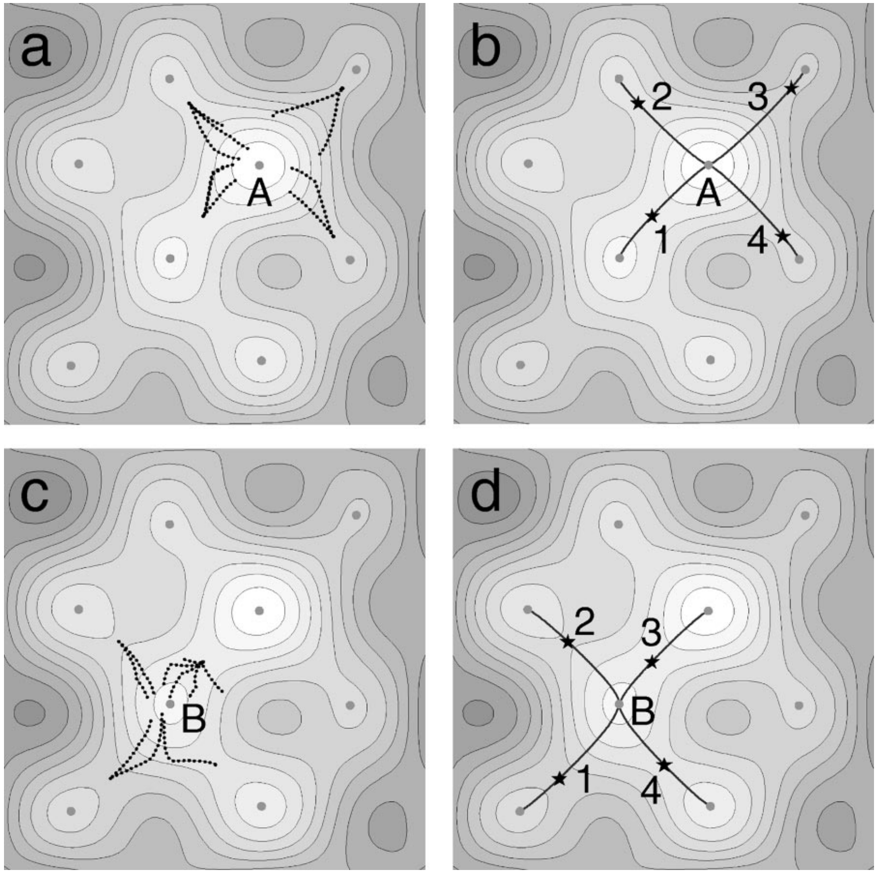
1.
ΔE = 0.23 eV
$\nu = 7 \cdot 10^{13}\ s^{-1}$

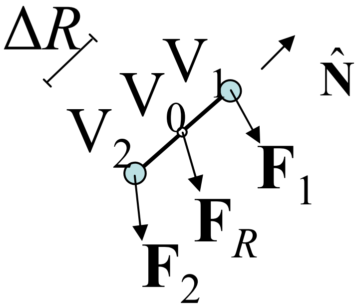
2.
ΔE = 0.37 eV
$\nu = 5 \cdot 10^{13}\ s^{-1}$

3.
ΔE = 0.41 eV
$\nu = 2 \cdot 10^{15}\ s^{-1}$

4.
ΔE = 0.44 eV
$\nu = 3 \cdot 10^{14}\ s^{-1}$





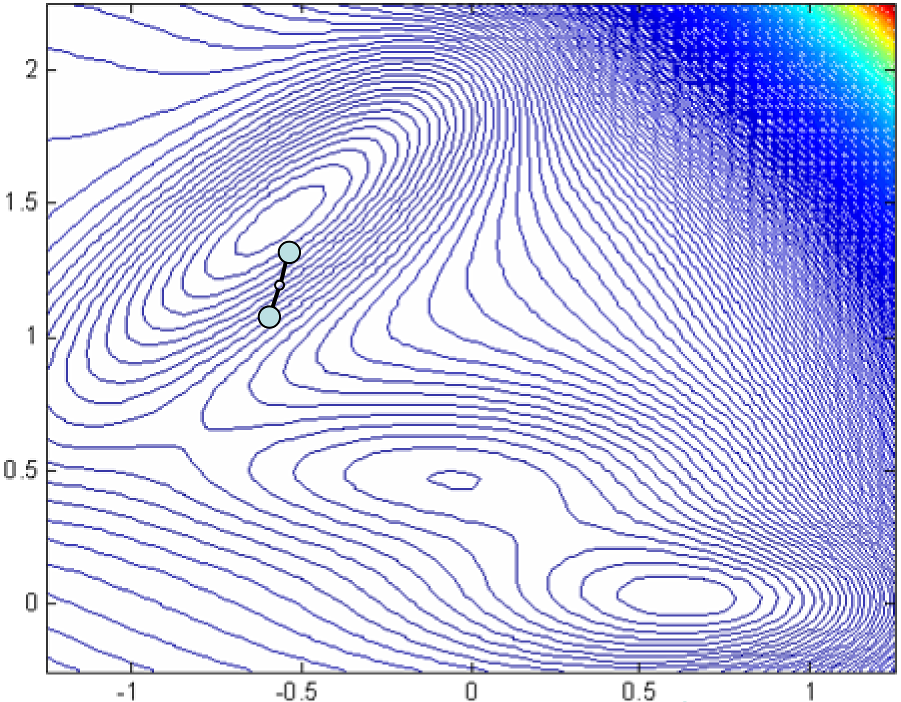


Dimer Method

[Henkelman & Jónsson 1999]

- Dimer energy: $E = V_1 + V_2$
- Curvature along Dimer:

$$C = \frac{E-(2V_0)}{(\Delta R)^2}$$



1. Estimate:

$$\mathbf{F}_1 = -\nabla V_1 \quad \mathbf{F}_2 = -\nabla V_2$$

$$V_0 = \frac{E}{2} + \frac{\Delta R}{4}(\mathbf{F}_1 - \mathbf{F}_2)\bullet\hat{\mathbf{N}}$$

$$\mathbf{F}_R = (\mathbf{F}_1 + \mathbf{F}_2)/2$$

$$\mathbf{F}^{\perp} = \mathbf{F}_1^{\perp} - \mathbf{F}_2^{\perp} \quad \mathbf{F}^{\|} = (\mathbf{F}_1^{\|} + \mathbf{F}_2^{\|})/2$$

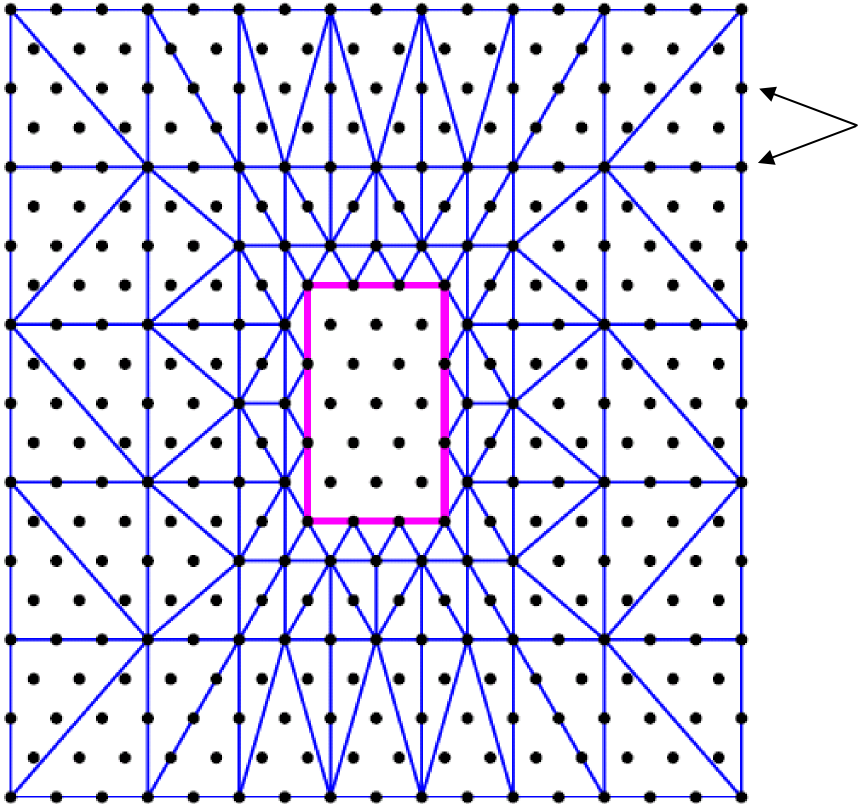
2. Dimer rotates to find the lowest curvature mode of PES, i.e. minimize Dimer energy
3. Translate Dimer towards ‘uphill’ according to

$$\mathbf{F}^{\dagger} = \begin{cases} -\mathbf{F}^{\|} & \text{if } C > 0 \\ \mathbf{F}_R - 2\mathbf{F}^{\|} & \text{if } C < 0 \end{cases}$$

4. Repeat

Quasicontinuum (QC) Method

- Based on the full *atomistic* model, use *mesh* to reduce the *degrees of freedom*



representative atoms
(*repatoms*)

QC Method

- ❑ Displacement of atom *i*: $\boldsymbol{x}_i = \boldsymbol{X}_i + \boldsymbol{u}_i$
- ❑ Displacement of N atoms: $\{\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_N\}$
- ❑ Empirically the total energy is the sum of site energy of each atom

$$E^{tot} = \sum_{i=1}^{N} E_i(\boldsymbol{u})$$

- ❑ the Stillinger-Weber (SW) type *site energy* for atom *i* is

$$E_i = E_i^{(2)} + E_i^{(3)}$$

with two-body potential $E_i^{(2)} = \frac{1}{2} \sum_{j \neq i} V_{ij}^{(2)}(r_{ij})$

and three-body potential $E_i^{(3)} = \frac{1}{6} \sum_{j \neq i} \sum_{k \neq (i,j)} V_{ijk}^{(3)}(\boldsymbol{r}_{ij}, \boldsymbol{r}_{ik})$

where $\boldsymbol{r}_{ij} = \boldsymbol{x}_j - \boldsymbol{x}_i$

QC Method

- The *total potential* energy of the system (*atoms* + *external loads*) is

$$\Phi(\boldsymbol{u}) = E^{tot}(\boldsymbol{u}) - \sum_{i=1}^{N} \boldsymbol{f}_i \boldsymbol{u}_i$$

  where $-\boldsymbol{f}_i\boldsymbol{u}_i$ is the potential energy of the applied load $\boldsymbol{f}_i$ on atom i

- The goal of the static QC method is to find the atomic displacements that minimize the *total potential* such that
  - the number of degrees of freedom is substantially reduced from $3N$;
  - the computation of the total potential is accurately approximated without the need to explicitly compute the site energy of all the atoms;
  - the critical regions can evolve with the deformation by addition/removal of repatoms.

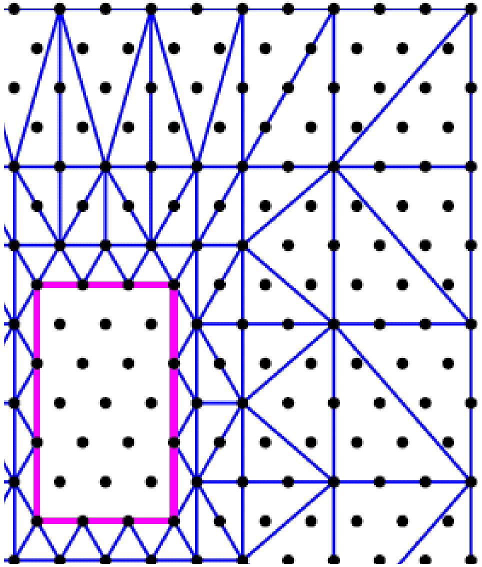
QC Method – Reduce DoF

- Any atom not chosen as a repatom is constrained to move according to the interpolated displacements
- This first approximation of the QC then, it to replace the energy E^{tot} by $E^{tot,h}$:

$$E^{tot,h} = \sum_{i=1}^{N} E_i(\boldsymbol{u}^h)$$

- with continuum displacement field

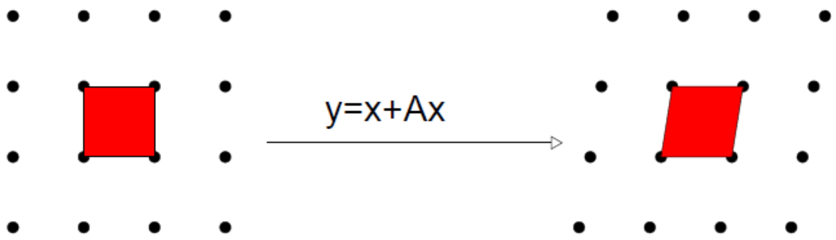
$$\boldsymbol{u}^h = \sum_{\alpha=1}^{N_{rep}} S_\alpha \boldsymbol{u}_\alpha$$



where S_α is the interpolation function with *local support*

QC Method – Local Energy

- The *Cauchy-Born rule* assumes that a uniform deformation gradient at the macro-scale can be mapped directly to the same uniform deformation on the micro-scale.



- Thus, every atom in a region subject to a uniform *deformation gradient* $F(X) \equiv \frac{\partial x}{\partial X} = I + \frac{\partial u}{\partial X}$ will be energetically equivalent.
- The energy within an element in crystals can be estimated by computing the energy of ***one*** atom in the deformed state and multiplying by the number of atoms in the element.
- *Energy density* for each element is

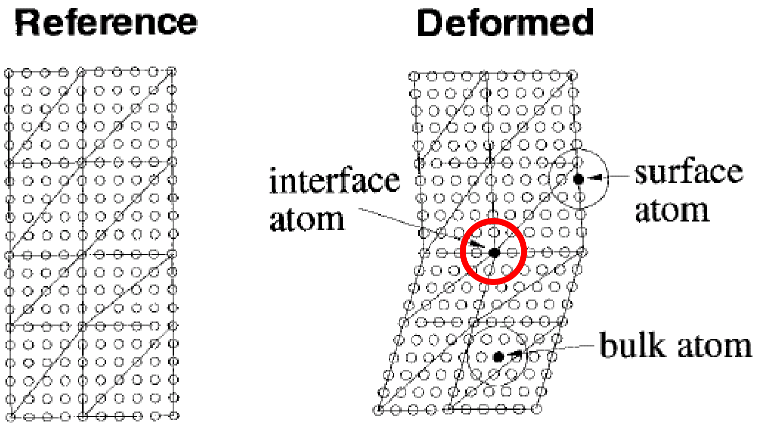
$$\mathcal{E}(F) = \frac{E_0(F)}{\Omega_0}$$

where Ω_o is the unit cell volume and E_o is the energy of the unit cell when its lattice vectors are distorted according to ***F***

- The total energy of an element is $E^{tot,h} \approx E^{tot,h'} = \sum_{e=1}^{N_{element}} \Omega_e \mathcal{E}(F_e)$

QC Method – Nonlocal Energy

- Local energy does not approximate well where deformation of crystal is non-uniform (e.g. surfaces and interfaces) and shorter than the cut-off radius of inter-atomic potential.



- **Energy-based formulation**: Nonlocal energy is *weighted sum* of those of repatoms as

$$E^{tot,h} \approx E^{tot,h'} = \sum_{\alpha=1}^{N_{rep}} n_\alpha E_\alpha(\boldsymbol{u}_h) \quad \text{where} \quad \sum_{\alpha=1}^{N_{rep}} n_\alpha = N$$

- **Force-based formulation**: The force on repatom β is determined by its neighborhood $\mathcal{C}_\beta$ (α,β,… for repatom)

$$\boldsymbol{f}_\alpha \equiv \frac{\partial E^{tot,h}}{\partial \boldsymbol{u}_\alpha} = \sum_{i=1}^{N} \frac{\partial E_i(\boldsymbol{u}^h)}{\partial \boldsymbol{u}^h} \frac{\partial \boldsymbol{u}^h}{\partial \boldsymbol{u}_\alpha} \implies \boldsymbol{f}_\alpha \approx \sum_{\beta}^{N_{rep}} n_\beta \left[\sum_{c \in \mathcal{C}_\beta} \boldsymbol{g}_c S_\alpha(\boldsymbol{X}_c) \right]$$

Atomic-level force in neighborhood ***c*** of repatom α

$$\boldsymbol{g}_c = \frac{\partial E^{tot,h}}{\partial \boldsymbol{u}^h_c}$$

$$\frac{\partial \boldsymbol{u}^h}{\partial \boldsymbol{u}_\alpha} = S_\alpha$$

"weights" of the atomic forces

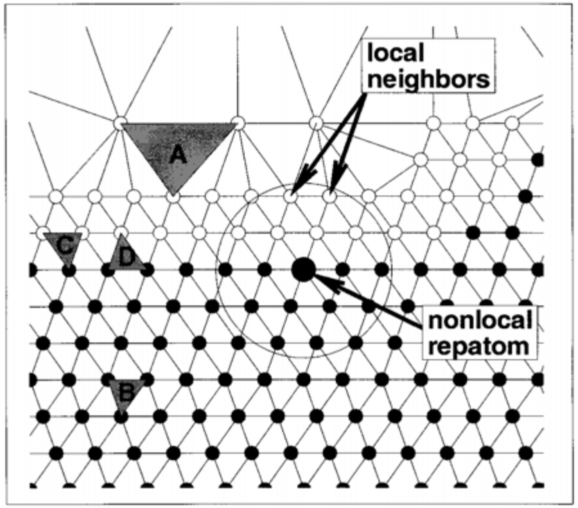
QC Method – detailed issues

- Local-nonlocal energy coupling

$$E^{tot,h} \approx \sum_{\alpha=1}^{N_{nl}} n_\alpha E_\alpha(\boldsymbol{u}_h) + \sum_{\alpha=1}^{N_{loc}} n_\alpha E_\alpha(\boldsymbol{u}_h)$$

where $N_{loc}+N_{nl}=N_{rep}$

- Local/nonlocal criterion: whether a repatom should be local or nonlocal?
  - whether there is significant variantion of the deformation gradient

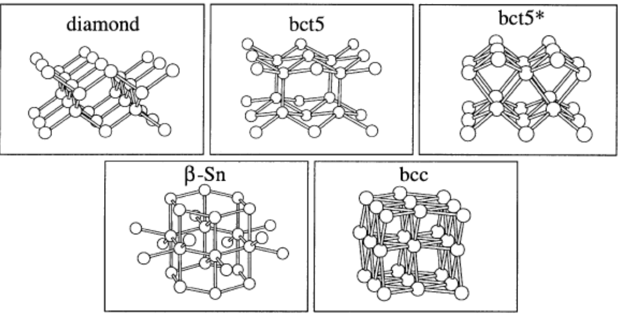


- Effects of local-nonlocal interface:
- Polycrystals
- Elastic/plastic deformation decomposition

QC Applications – nanoindentation

(Smith et al. 2001)

- **Silicone**
- Phase transformation and dislocation nucleation observed
- Different phases observed



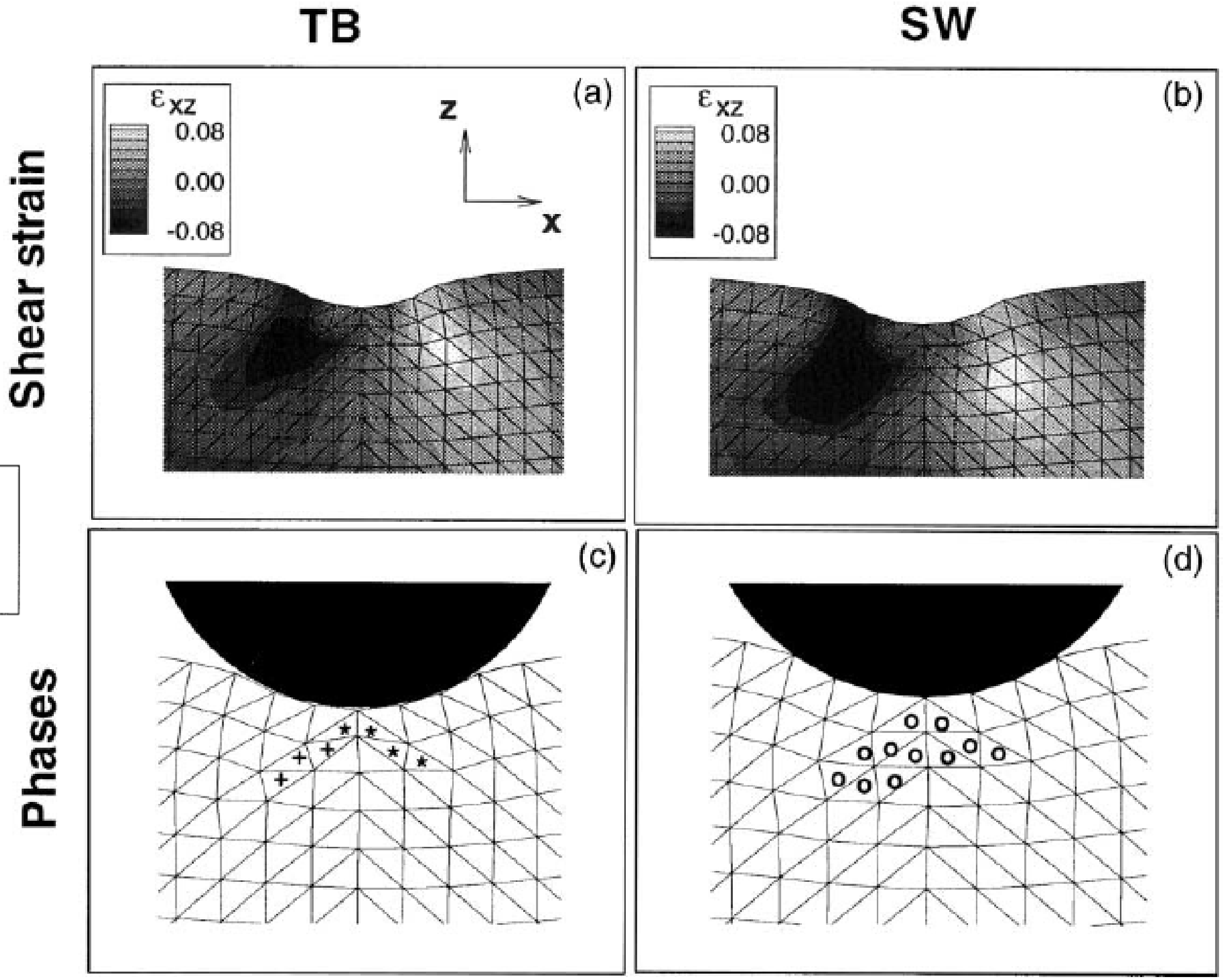
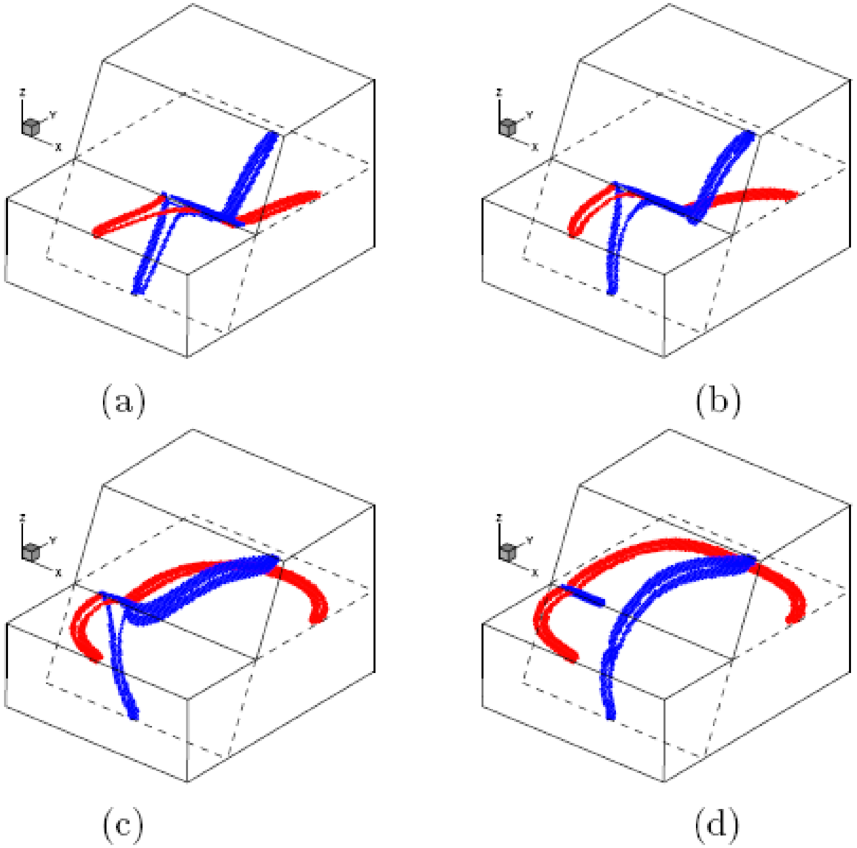


Fig. 3. Comparison of snapshots of the 2D finite element mesh after phase transformations have begun. Results using the Stillinger–Weber (SW) potential and a tight-binding (TB) Hamiltonian are shown. The figures show the shear strain ϵ_{xz} ((a) and (b)), and the phases that have formed ((c) and (d)). In (c) and (d), the symbol ○ indicates the bct5 phase, the symbol $*$ indicates the bcc phase, and the symbol + indicates the bct5* phase (see Fig. 4). Blank finite elements remain in the diamond phase. The indenter is shown as the black regions in (c) and (d).

QC Applications – dislocation behavior

(Rodney & Phillips 1999)

- Dislocation junction under shear stress

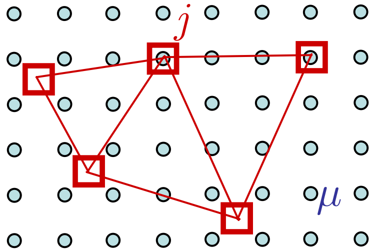

(a) (b)

(c) (d)

FIG. 2. Sequence of snapshots of the junction geometry under increasing stress. (a) Zero applied stress, (b) stress is 0.011μ, (c) stress is 0.018μ just before the junction breaks, (d) stress is 0.018μ at the end of the simulation.

Coarse Grained (CG) Molecular Dynamics

- displacement of mesh node *j* (does not have to coincident with an atom) $\mathbf{u}_j = \sum_\mu f_{j\mu}\mathbf{u}_\mu$, is a weighted average of displacements of atoms μ's.



- Displacement field $\mathbf{u}(\boldsymbol{x}) = \sum_j N_j(\boldsymbol{x})\mathbf{u}_j$

- Coarse grained energy is the average of the canonical ensemble of the atomistic Hamiltonian on the constrained phase space {(**x**,**p**)}

$$E\left(\mathbf{u}_k, \dot{\mathbf{u}}_k\right) = \langle H_{MD}\rangle_{\mathbf{u}_k,\dot{\mathbf{u}}_k} = \int d\mathbf{x}_\mu d\mathbf{p}_\mu H_{MD} e^{-\beta H_{MD}} \Delta / Z$$

where β=1/(*kT*), $Z = \int d\mathbf{x}_\mu d\mathbf{p}_\mu e^{-\beta H_{MD}} \Delta$ is *partition function*, and

$\Delta = \prod_j \delta\left(\mathbf{u}_j - \sum_\mu \mathbf{u}_\mu f_{j\mu}\right) \delta\left(\dot{\mathbf{u}}_j - \sum_\mu \mathbf{p}_\mu f_{j\mu} / m_\mu\right)$ enforces constraints.

- The atomistic Hamiltonian

Cohesive energy of atoms

$$H_{MD} = \sum_\mu \frac{\mathbf{p}_\mu^T \cdot \mathbf{p}_\mu}{2m} + \sum_\mu E_\mu^{coh} + \sum_{\mu,\nu} \frac{1}{2}\mathbf{u}_\mu^T \cdot D_{\mu\nu} \cdot \mathbf{u}_\nu$$

CGMD

- Partition function $Z = Z_{kin} Z_{pot}$
- Potential part of partition function is

$$Z_{pot}(\mathbf{u}_k, \beta) = C_1 C_2 \beta^{-\frac{3}{2}(N_{atom} - N_{node})} e^{-\frac{1}{2}\beta \mathbf{u}_j^T \cdot K_{jk} \cdot \mathbf{u}_k}$$ w/ stiffness $K_{jk} = (\sum_{\mu,\nu} f_{j\mu} D_{\mu\nu}^{-1} f_{k\nu})^{-1}$

- CG potential energy then is

$$E_{pot}(\mathbf{u}_k) = -\partial_\beta \log Z_{pot} = \underbrace{\frac{3}{2}(N_{atom} - N_{node})kT}_{\text{Thermal}} + \underbrace{\frac{1}{2}\mathbf{u}_j^T \cdot K_{jk} \cdot \mathbf{u}_k}_{\text{Harmonic}}$$

- Computationally, the full CG energy is

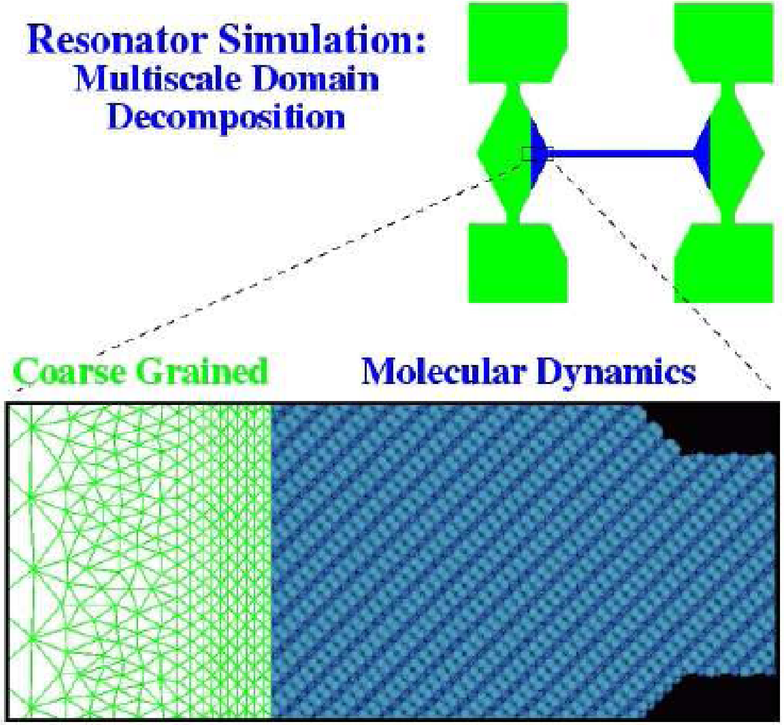
$$E\left(\mathbf{u}_k, \dot{\mathbf{u}}_k\right) = U_{\text{int}} + \frac{1}{2}\sum_{j,k}(M_{jk}\dot{\mathbf{u}}_j^T \cdot \dot{\mathbf{u}}_k + \mathbf{u}_j^T \cdot K_{jk} \cdot \mathbf{u}_k)$$

where $U_{\text{int}} = N_{atom} E^{coh} + 3(N_{atom} - N_{node})kT$ is internal energy

and $K_{jk} = (\sum_\mu f_{j\mu} m_\mu^{-1} f_{k\mu})^{-1} = \sum_\mu m_\mu N_j(\boldsymbol{x}_\mu) N_k(\boldsymbol{x}_\mu)$ is CG mass matrix

CGMD Applications – MEMS/NEMS

- NEMS silicon micro-resonator
  - The coarse grained (CG) region comprises most of the volume
  - The molecular dynamics (MD) region contains most of the simulated degrees of freedom
  - the CG mesh is refined to the atomic scale where it joins with the MD lattice.



Summary

- First-Principles MD
- On-the-fly KMC
- Quasicontinuum method
- Coarse-Grain Molecular Dynamics

Space

Time

Further Readings

First-Principles Molecular Dynamics

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